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ESTIMATION OF BORON GLAZE ON EDMITE IGNITER COMPOSITION

by

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ABSTRACT

The method described in FRL-TN-85 (1) for the determination of the boron content of organoborane compounds has been adapted to the estimation of the percentage of boron in boron-glazed Eimite igniter composition. About 6 hours of elapsed time are required, of which 5 are working time, for the performance of a duplicate pair of runs. The average agreement between duplicate runs is 0.04% of the sample.

CONCLUSIONS

1. A method has been developed for determining the percentage of boron in boron-glazed Eimite igniter composition. (2). It is a modification of the method described in FRL-TN-85 (1).

2. Approximately 6 hours are required of which 5 are working time, for the performance of a duplicate pair of runs. The average agreement between duplicate runs is 0.04% of the sample.

RECOMMENDATIONS

1. The method described in this report should be adopted for the determination of the percentage of boron in boron-glazed Eimite igniter Compositions.

INTRODUCTION

The application of a glaze of boron has been found to impart improved properties to Eimite Igniter Composition. This composition is described in Purchase Specification AE 1-54 (2) which requires that the glaze constitute 2 $\pm$ 1% of the weight of the total material, and that the resultant glazed finish be evident on visual inspection. Needless to say, a convenient method for quantitative measurement of the percentage of boron represented by the glaze is much to be preferred over a purely qualitative observation.

It is desirable that any method, particularly one to be included in a specification, be reasonably rapid and reproducible, easily performed, and not require highly specialized equipment.

A recently-reported method for determining the boron content of organo-borane compounds (1) appeared to satisfy these general requirements for a specification method and to be of very broad scope. Only a modification of the details of this method was necessary to adapt it to the estimation of the boron content of the glazed Eimite composition for which it has been found well-suited. The steps in the modification process and the final modified procedure are described in this report.

RESULTS AND DISCUSSION

The several steps in the adaptation of the method of FRL-TN-85 to the analysis of boron-glazed Eimite should be apparent on inspection of Table I. As successive samples were received progressive changes were made until a modified procedure had been evolved utilizing the same principles but especially suited to the analysis of this composition.

The often sensitive nature of the organoborane preparations to be analyzed by the method of FRL-TN-85, and the frequently small quantities synthesized, limited the specimens to be analyzed by that method to 0.02 grams. Since the boron-glazed Eimite exhibits no such tendency to explosive decomposition, and since the quantity of sample submitted is generally large, it is possible to increase the weight of specimen from 0.02 to 1 gram, with a resulting increase in titration from about 0.4 to 7 ml. of barium hydroxide. Such a change is obviously in the interest of increased "signal-to-noise ratio".

The tendency for the apparent boron content to decrease as the specimen weight increases indicates that there is a definite factor of error operating which becomes relatively small and may be neglected if the specimen taken is at least 0.3 gram.

The lower sensitivity also makes possible the elimination of one of the more tedious steps of the FRL-TN-85 procedure - the addition of the digestion acids, milliliter by milliter, to allow time for reaction between each increment. Instead the acids are pre-mixed and the total amount required is added in a single portion. Unfortunately, the potassium dichromate used to signal completion of digestion cannot be incorporated into the acid mixture because of its insolubility; and therefore, must still be added separately.

Mention has been made of the increased digestion temperature, indicated in Table I by the rate of reflux. In FRL-TN-85 the temperature was limited to the low level corresponding to a drop of reflux every 5 minutes. For the analysis of boron-coated Eimite it was found possible to increase the temperature to the maximum attainable on a Lindberg hot plate (4 seconds per drop), without any tendency to decompose violently. To avoid both loss of boron and discharge of perchloric acid vapor, the digestion flask is protected by an air-condenser. Pre-heating on the steam bath was tested in the case of Sample 30 but judged to be of no advantage and was not included in the final procedure. The treatment finally adopted consists of 30 minutes of heating on this hot plate with a 1/8-inch thickness of asbestos board under the flask (15 seconds per drop) followed by heating directly on the hot plate (4 seconds per drop) until completion of the process is indicated by a change of color from green to the orange characteristic of dichromate. The latter phase required 10-20 minutes. Although the weight of sample taken is much greater than that used in FRL-TN-85 (1 g. vs 0.02 8) the increased temperature results in a decrease of digestion time from 1½-2 hours to less than an hour.

To estimate the precision of the procedure finally evolved, 6 replicate determinations were performed on one of the samples (No. 30), with results shown in Table II. The barium hydroxide-solution was standardized for each replicate determination. The agreement is very satisfactory, with an average difference between runs of 0.04% boron. Application of a Studentized Range Table (3) shows a 95% probability that duplicate runs will agree within 0.12. In routine analytical practice, agreement would be expected to be even better, since a common standardization would ordinarily be performed for each series of runs, eliminating the standardization component of the error. Since the objective of the manufacturing process is to apply a coating of boron equal to $2 \pm 1\%$ of the weight of the base grain, and since the boron used is known to be of about 80% purity, the average percentage of boron found is almost exactly what should be expected. About six hours of elapsed time, five of which are working time, are required for the performance of a duplicate pair of runs of a single sample. An economy of working time would result if several samples were analyzed simultaneously.

EXPERIMENTAL PROCEDURE

Special Apparatus:

pH meter equipped with glass-calomel electrode system, and calibrated with pH7 buffer.

Buret, 10 ml., graduated at 0.05 ml. intervals.

Hot plate, 11 Watts/sq. inch, Lindberg Type H-2 or equivalent.

Special Materials:

Barium hydroxide solution, prepared by steeping 3 grams of barium hydroxide octahydrate in a liter of water at least overnight, then filtering through a Whatman No. 12 or equivalent folded paper.

Boric acid, standard solution containing 0.17 mg. of boron per ml., prepared by dissolving an accurately weighed 0.5 gram portion of boric acid in 500 ml. of water.

Hydrochloric acid, 1N solution.

Mixed acid, prepared by stirring 33 ml. of 71% perchloric acid into 12 ml. of water, and into this, stirring 55 ml. of 96% sulfuric acid. This mixture must be permitted to cool before use.

Potassium dichromate, 2% solution.

Sodium hydroxide, 2N solution, freshly prepared.

Determination:

Accurately weigh a 1-gram specimen into a 250-ml. erlenmeyer flask with standard-taper joint and insert an air-condenser. Through the condenser add 1 ml. of potassium dichromate solution and, slowly, 10 ml. of mixed acid. Make similar additions to a sample-free (blank) flask (Note 1). Heat for a half-hour at a reflux rate of 3-4 drops per minute (Note 2), then increase the temperature to a rate of 10-15 drops per minute and hold at this temperature until the color of the contents changes from green to orange. Remove the flasks and let them cool to room temperature. Wash the condenser walls and base with water and transfer the contents of the flask to a 250-ml.

volumetric flask. Add water to bring the volume to the mark and shake to mix.

Transfer a 25-ml. aliquot from the volumetric flask to a 150-ml. erlenmeyer flask with a standard-taper joint. From a 10-ml. Mohr pipet, add 8 ml. of freshly-prepared 2N sodium hydroxide solution, a strip of litmus paper (Note 3), and more sodium hydroxide solution dropwise until the paper just turns blue. Wash the flask mouth and walls with water. Add 1N hydrochloric acid a drop at a time until the color of the litmus paper just reverts to red, and then one drop more. Attach the flask to a water-cooled condenser, reflux for 15 minutes, then remove the flask and place it in a cold-water bath (Note 4).

When cool, wash the contents of the flask into a 150-ml. beaker and insert the electrodes of the pH meter (Note 5). From the 10-ml. buret add barium hydroxide solution (the volume need not be recorded) in increments of about 1 ml. to pH 4; 0.5 ml. between pH 4 and pH 5, 0.25 ml. between pH 5 and pH 6, and 0.1 ml. between pH 6 and pH 6.7. When the pH exceeds 6.7, add only a drop at a time, allowing 30 seconds between drops, until the pH is adjusted to 7.2. Add 5 grams of mannitol and measure the volume of barium hydroxide solution required to restore the pH to 7.2, adding the solution in progressively smaller increments in the manner already described. Standardize the barium hydroxide solution not earlier than the day before nor later than the day after that on which the titration was performed.

To standardize the barium hydroxide solution pipet 25 ml. of "blank" solution and 10 ml. of standard boric acid solution into a 150-ml. erlenmeyer flask with standard-taper joint. Adjust the acidity, reflux, and titrate in the manner described in the previous paragraphs. Calculate the strength of the solution as follows:

$$S = \frac{0.1750 W_1}{V_1}$$

S = Strength of barium hydroxide solution, mg. of boron per ml.

Where:

V_1 = Volume of barium hydroxide solution required to titrate the aliquot of boric acid, ml.

W_1 = Weight of boric acid in the aliquot of boric acid solution, mg.

Calculate the boron content of the sample as follows:

$$\text{Boron, \%} = \frac{100 V_2 S}{W_2}$$

Where:

S = Strength of barium hydroxide solution, mg. of boron per ml., (see previous paragraph).

V_2 = Volume of barium hydroxide solution required to titrate the aliquot of sample solution, ml.

W_2 = Weight of sample represented by the aliquot taken, mg.

Notes:

1. It is not necessary to include a blank with each run of samples. Blank solution from a recent (within a few weeks) run may be used provided that the quantity on hand is sufficient to standardize the barium hydroxide solution.

2. These temperatures may be attained on a Lindberg Type H-2 electric hotplate, first with and then without a thickness of 1/8" asbestos board.

3. If the paper should assume the blue shade, wash down the flask and reacidify with 1N hydrochloric acid solution as described subsequently. In later runs decrease the volume of 2N sodium hydroxide solution added at this point.

4. A vessel containing dry ice in contact with water makes a satisfactory bath.

5. The use of a magnetic stirrer will facilitate subsequent operations. In the event that such a stirrer is used the housing of the motor and the shielding of the pH meter should both be connected to ground.

REFERENCES

1. R.M. Abbott, N.M. Liszt, and M. Roth, "Estimation of the Boron Content of Organo-Decaborane Compounds". Technical Note FRL-TN-85, Picatinny Arsenal, Dover, New Jersey, September 1961.

2. Purchase Specification AE 1-54 (Rev. 1), Picatinny Arsenal, Dover, New Jersey, 16 August 1960.

3. C.A. Bennett and N.L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry". John Wiley & Sons, Incorporated, New York, 1954, Table 5.8.

TABLE I

Percentages of Boron in Glazed Eimite Determined Under Various Conditions

Sample No.	Sample Weight, g.	Acids added	Steam bath preheat	Reflux: Time per drop	Reflux: Period, hours	$Ba(OH)_2$ ml.	Boron, % [a]
	0.02	separately	no	5 min.	2.0	0.4	3.72
135	0.02	"	no	5 min.	1.5	0.4	3.36
(1960)	0.05	"	no	5 min.	1.5	0.6	2.63
	0.05	"	no	5 min.	1.5	0.7	2.45
	0.1	premixed	no	5 min.	<1.0	0.8	2.00
PI-E-305	0.3	"	no	5 min.	<1.0	1.9	1.65
(1962)	0.1	"	no	4 sec.	<0.2	1.0	2.40
	0.3	"	no	4 sec.	<0.2	1.9	1.59
	0.3	"	30 min.	15 sec.	0.1	1.7	1.37
30	1.	"	30 min.	15 sec.	0.6	6.7	1.62
(1962)	0.3	"	no	15 sec.	0.2	2.0	1.76
	1.	"	no	15 sec.	0.9	6.9	1.66

[a] Calculated on an as-received basis.

TABLE II

Replicate Determination of Boron Glaze

Boron, % (as received):	Results
Run 1	1.60
Run 2	1.62
Run 3	1.56
Run 4	1.65
Run 5	1.62
Run 6	1.65
Average	1.62
Average pair difference	0.040
Degrees of freedom	5
Standard diviation	0.034
Duplicate range, 95% limit	0.12

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2. Boron — Determination

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II. Eimite

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